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FUNCTIONAL MEMBRANES. PRESENT AND FUTURE

Toyoki KUNITAKE

(NASA-TM-76667) FUNCTIONAL MEMBRANES.  
PRESENT AND FUTURE (National Aeronautics and  
Space Administration) 24 p HC A02/MF A01

N82-20256

CSSL 07D

Unclas

G3/25 09392

Translation of "Yuki Gosei Kagaku Kyokaishi", Vol. 39, No. 6,  
1981, pp. 477-486



NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  
WASHINGTON, DC 20546 JANUARY 1982

## STANDARD TITLE PAGE

1. Report No. NASA TM-76667		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle FUNCTIONAL MEMBRANES. PRESENT AND FUTURE				5. Report Date January 1982	
				6. Performing Organization Code	
7. Author(s) Toyoki Kunitake Dept of Organic Synthesis, Faculty of Engineering Kyushu University				8. Performing Organization Report No.	
				10. Work Unit No.	
9. Performing Organization Name and Address Leo Kanner Associates, Redwood City, California 94063				11. Contract or Grant No. NASW-3541	
				13. Type of Report and Period Covered Translation	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration, Washington, D.C. 20546				14. Sponsoring Agency Code	
15. Supplementary Notes Translation of "Yuki Gosei Kagaku Kyokaishi," Vol. 39, No. 6, 1981, pp. 477-486					
16. Abstract The present situation and the future development of the functional membrane are discussed. It is expected that functional membranes will play increasingly greater roles in the chemical industry of the coming decade. These membranes are formed from polymer films, liquid membranes or bilayer membranes. The two most important technologies based on the polymeric membrane are reverse osmosis and ion exchange. The liquid membrane is used for separation of ionic species; an extension of the solvent extraction process. By using appropriate ligands and ionophores, highly selective separations are realized. The active transport is made possible if the physical and chemical potentials are applied to the transport process. More advanced functional membranes may be designed on the basis of the synthetic bilayer membrane.					
17. Key Words (Selected by Author(s))			18. Distribution Statement Unclassified-Unlimited		
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of Pages	
				22.	

Toyoki Kunitake

Dept. of Organic Synthesis, Fac. of Eng. Kyushu Univ.

### 1. Introduction

Great things are expected of functional membranes. The role of functional membranes is expected to increase in fields including resources, energy and environment in the 1980's. Examples include recovery using liquid membranes of wet type alloys and precious metals, beginning with uranium, from the sea and concentration of uranium 235 by ion exchange membranes in the field of resources, effective utilization of solar energy, highly efficient, selective gas-liquid separation in the field of energy and highly sensitive sensors in the field of the environment. It is difficult to determine which of these functional membrane technologies is directly applicable to organic synthetic chemistry. Thus, we will explain the present circumstances involving functional membranes and future developmental trends without dealing with that question.

### 2. Functional Polymer Membranes

Functional membranes can be classified into three types based on the material (medium). They are polymer membranes (solid membranes), liquid membranes and bilayer membranes. We will discuss polymer membranes here. Nakagawa has summarized functional polymer membranes and their fields of application, and has cited the highest values of the various types of functions [1]. Table 1 reproduces the majority of the table of Nakagawa. Among these, conductive membranes, photosensitive membranes and optical membranes have no direct relation with the details of

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\* Numbers in the margin indicate pagination in the Japanese text.

this paper. Water- and solute permeable membranes and others below those pertain to the organic synthetic chemistry industry. The first water-solute permeable membrane is used in reverse osmosis, but this is a technique which has already been applied practically. Table 2 illustrates the many examples of application related to the synthetic chemical industry [2]. The range of application is broad, including production of pure water by purification of sea water or brackish water, separation-concentration-refining of products in the food industry, fermentation industry and drug industry, oil-water separation accompanying treatment of waste water in the petrochemical, pulp, fiber and food industries, recovery of valuable plants and reutilization of water etc.. The membranous materials begin with cellulose acetate, and in recent years, materials which can be used under severe conditions, including high temperatures and strong acidity, such as aromatic polyamides, polysulfonates and polybenzimidazolone have been developed.

Gas permeable membranes are used in separation of gas blends. The initial example was the hollow filament module for hydrogen separation which was developed by DuPont in 1968. This was produced to recover the non-reactive fraction of hydrogen used in desulfurization of petroleum. The membranous material was polyethylene terephthalate, and the helium recovery device developed subsequently in Japan was a hollow filament similarly using polyethylene terephthalate. In addition, PEG-bisphenyl A copolymer membranes have been tested for separation of  $H_2S$  from  $N_2$  and  $SO_2$  from  $N_2$  [1].

/478

Table 1 Functional polymer membranes and their industrial applications<sup>1)</sup>

Membrane function	Industrial application
conductive, semiconductive	solar cell, long-life cell, electronic device
photoconductive	photocopy, information storage
photosensitive, electron sensitive, X-ray sensitive	integrated circuit, metal processing, photo printing
pyroelectric, piezoelectric	senser, transducer
optical	optoelectronics
anti-radiation	insulating material for reactor, food preservation
permeation of water and other solutes	desalination, industrial water treatment
gas permeation	oxygen enrichment, hydrogen separation
permeation of organic liquids	separation of azeotropic mixtures
ion exchange	electrolysis, uranium enrichment
enzyme-bound	production of amino acids and saccharides, bioreactor
microorganism, antigen-antibody	biosenser
photochemical	water decomposition

Table 2 Applications of reverse osmosis<sup>2)</sup>

Specific field	Use
water production	pretreatment of industrial water, production of ultra-pure water
separation, concentration and purification	separation and concentration of amino acids treatment of fermentation mixtures
medical and medicinal	production of pure water
reclamation from spent water	recovery of lignin and xylose in pulp industry treatment of alcohol distillate, reagent recovery from photographic solutions
separation of oil and water	treatment of spent emulsion and petrochemical waste
textile	removal of dyes surfactants, etc from spent water

Separation of organic liquids using polymer membranes has long been examined on blends of styrene and ethylbenzene as well as blends of dienes and alkenes. Subsequently, the recovery of organic solvents from blends of organic solvents and water, from azeotropic blends and blends of organic liquids near the boiling point has been examined from the viewpoint of energy saving. For example, membranes with 92 wt.% of polyvinyl pyrrolidone grafted onto porous teflon have been discovered to be very effective in separation of water and dioxane [3].

Research into ion exchange membranes began in the 1950's, and they were developed in Europe and the United States primarily for desalination and purification of salt water, while in Japan, they were developed for salt production technology through electrodialysis of sea water.

The applicable technology of ion exchange membranes is based on the following three main principles according to Imoo [4]. The first is separation and recovery of solutes by diffusion dialysis utilizing the differences in concentrations of solutes. The second is the separation and recovery of solutes by electrodialysis utilizing electrical energy. The third is the production of oxidation-reduction products by the electrode reaction which occurs subsequently in electrodialysis. Table 3 summarizes typical examples of techniques based on those principles.

Continuous mass transfer through separation concentration-dilution diffusion of ions is easily implemented in electrodialysis, and neutral molecules and ions can be separated. Mutual separation and concentration of anions and cations with different signs can be effected simultaneously using a device with a multi-chamber structure which alternately combines cation exchange membranes and anion exchange membranes. One example is the case of the metathesis reaction by electrodialysis illustrated in figure 1 [5].



In addition, highly selective permeable membranes capable of separation-concentration of monovalent and polyvalent ions of the same sign have also been perfected. Monovalent anionic selective membranes have been formed from organic electrolyte thin membranes with cation exchange groups on the surface of conventional anion exchange membranes, and  $\text{Cl}^-$  (permeable) and  $\text{SO}_4^{3-}$  (non-permeable) could be separated by electrodialysis. Conversely, separation of  $\text{Na}^+$ ,  $\text{K}^+$  (permeable) and  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  (non-permeable) has been possible when organic electrolyte thin films with anion exchange properties have been formed on the surface of cation exchange membranes [4].

Ion selective permeability has been accomplished by combining ion exchange groups with reverse osmotic membranes, leading to the development of new ion selective permeable reverse osmotic membranes. Furthermore, the process combining ion exchange membrane electrodialysis and reverse osmosis for desalination of various types of salt solutions such as regenerated waste liquid of ion exchange resin has recently attracted attention.

/479

Table 3 Application of ion-exchange membranes<sup>1)</sup>.

Principle	Technology
1. dialysis	acid recovery from spent acids containing metal ions recovery of sulfuric acid in the production of caprolactam concentration-gradient cell using sea water
2. electrodialysis	salt production from sea water desalination metal recovery from spent electroplating solution
3. electrodialysis-electrode reaction	production of adiponitrile by electrolytic dimerization reduction of uranium production of alkali and chlorine

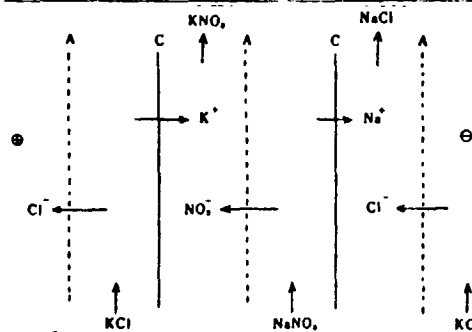
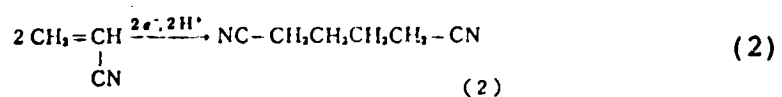


Fig. 1 Metathesis reaction by electrodialysis.

C: cation exchange membrane  
A: anion exchange membrane

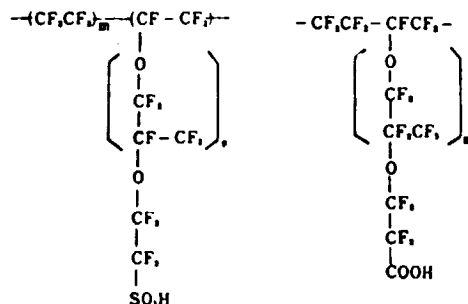
One example of the third principle, specifically an example of combination of electrodialysis and the electrode reaction, is the production of adiponitrile.





Two types of methods have been developed, the Monsanto method [6] and the method of Asahi Kasei [7], and salts with high conductivity and little affinity for oily phases such as ammonium sulfate are used as the electrolytic supporting electrolyte in the emulsion method of Asahi Kasei. It is an outstanding industrial process since the emulsion following the reaction is physically destroyed while only the oily phase is separated and adiponitrile is recovered.

Nafion membrane of DuPont and fluorocarboxylic acid membrane of Asahi Kasei are typical ion exchange membranes for producing salt electrolytic soda.



Nafion membrane of DuPont  
 $m = 5-13.5$ ,  $z = 1, 2, 3..$

membrane of Asahi Kasei

### 3. Liquid Membrane and Selective Transport Membranes

The separation and concentration of many neutral molecules and of ions are possible through polymer membranes typified by reverse osmosis membranes and ion exchange membranes, but the separation mechanism is controlled by physical factors including incorporation (dissolution) in the membrane and diffusion.

Specific interactions between the membrane media and the chemicals to be separated must arise for specific separation and transport by membranes. Numerous conditions must be fulfilled to achieve the objectives of liquid membranes. Here, selective separation of ions by liquid membranes is first explained based on the explanation [9] summarized by Takagi and Ueno.

The solvent extraction method, in which the target ions are converted into a selective neutral chemical form and then extracted in organic solvent to separate ions dissolved in aqueous solutions, has long been known, but combination of two stages of extraction, in which the ions extracted in organic solvent are converted into water soluble form and then reextracted in aqueous solution, is the basic principle in ion separation by liquid membranes. Figure 2 illustrates schematically the course of separation of pyridinium ions as a simple example of this. Specifically, pyridinium ions of aqueous phase A are neutralized by NaOH and incorporated in the organic liquid membrane followed by reaction with HCl, forming pyridinium ion which is then extracted in aqueous phase B. The net reaction is a neutralization reaction of NaOH and HCl, and this is the driving force between ion transport.

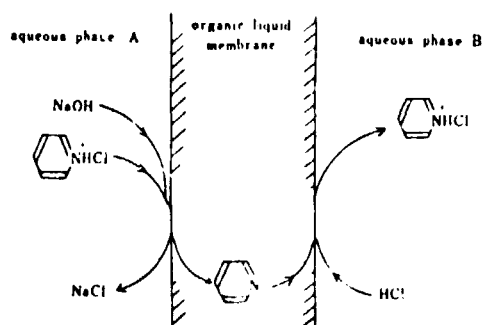
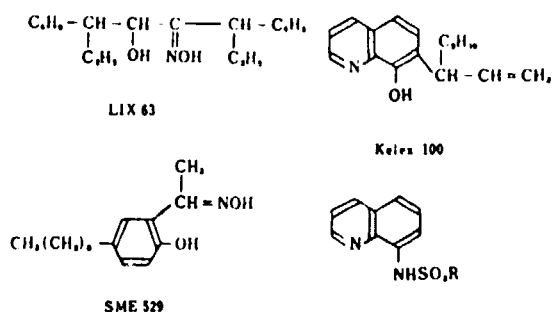


Fig. 2 Separation of pyridinium ion by a liquid membrane.

Various types of separation are possible by inducing reactions at the membrane interface. The types of extraction reactions (transport) are categorized as follows.

3.1 Transport of Molecules without Charge based on Simple Distribution Equilibrium The selectivity in this case is not great since extraction is accomplished only by the difference in solubility of the aqueous phase in relation to the liquid membrane.

3.2 Transport by Metal Chelate Formation Metal chelates in which oxine and  $\beta$ -diketone are the ligands have solubility similar to that of conventional organic compounds since they have no charge and since the covalent bonding of metal ligand bond is strong. Consequently, these ligands are used in extraction of metal ions from the aqueous phase. Ligands with high fat solubility due to alkyl group substitution as illustrated below are used to efficiently implement membrane permeation [10].



8-sulfonamidoquinolin

Selective ion transport is possible due to the differences in the ligand structure.

### 3.3 Transport of Metal Ions by Non-Chelate Reagents

Aliphatic carboxylic acids with great fat solubility and dialkyl phosphoric acids do not form constant chelate structures in relation to metal ions. Aqueous phase metal ions are extracted in organic phase as associated substances composed of multiple molecules and are transported.

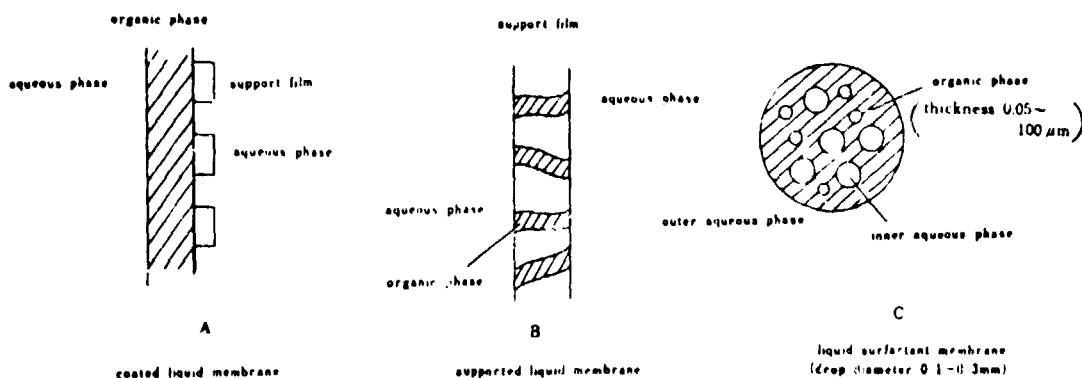


Fig. 3 Uses of liquid membranes.  
The organic phase is indicated by shadowing.

3.4 Transport by Ion Pairs Transport of ions in organic liquid membranes is possible by formation of ion pairs with great hydrophobicity. Transport of  $\text{HCl}$ ,  $\text{HClO}_4$  and  $\text{H}_2\text{SO}_4$  etc. would be possible if amines with long chain alkyl groups such as Amberlite LA-1 or trioctylamine were used. That is because even anions with intense hydrophilicity such as  $\text{Cl}^-$  or  $\text{SO}_4^{2-}$  would be dissolved in organic layers in the form of ion pairs since the fat solubility of  $\text{R}_3\text{NH}^+$  cations is great. The transport of  $\text{UO}_2(\text{NO}_3)_2$  by tributyl phosphoric acid is believed to occur by a similar mechanism.

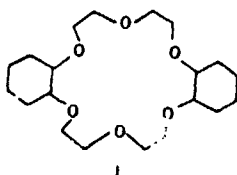
Coating or immersion in polymer films or the use of emulsified liquid membranes are typical methods when organic liquid membranes are actually used. Figure 3 illustrates this schematically. A is the case in which plasticizer containing

/481

extraction reagents is coated on filter paper or a net of synthetic fibers. B is the case in which organic liquids are immersed in porous membranes of polymer material rendered more readily dampened by organic solvents such as polypropylene or teflon. The emulsification liquid membrane is obtained using a suitable surfactant by first producing a water-in-oil emulsion followed by suspending this in an aqueous phase. This method has rapid diffusion of solute since the reaction surface area is large and the fluidity of the liquid membrane is good. This is the liquid membrane system most promising industrially at present.

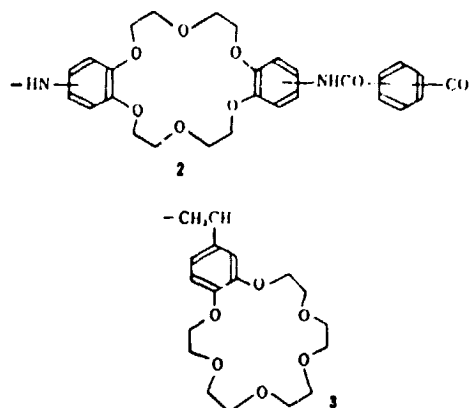
Selective transport of metal ions can be carried out quite specifically by metal chelate or ion pairs, but ionophores can be cited as ligands with outstanding development [11]. Examples in biological systems include Valinomycin, which is a cyclic oligopeptide, as well as cyclic and non-cyclic polyesterether ketones such as Nonactin, Monensin and X 537 A. All transport metal ions effectively in vital membranes by large cyclic conformations which centripetally incorporate metal ions and oleophilic outer walls.

Crown ether presented by C.J. Pedersen in 1967 is a typical synthetic ionophore. For example, since dicyclohexyl-18-crown-6 **1** can incorporate  $K^+$  well,  $KMnO_4$  can be rendered soluble in benzene. The diameter of the internal pores varies with the number of cyclic members of crown ether, and selective incorporation of alkali metal ions ( $Na^+$ ,  $K^+$ ,  $Tb^+$ ,  $Cs^+$ ) is possible.



Chain like polyethers as well as crowns which are cyclic polyethers exhibited selectivity toward metal ions. Moreover, implementation of selective incorporation of heavy metal ions due to replacement of ether oxygen by nitrogen or sulfur as well as the development of polycyclic cryptands\* have been marked in this field. Here, we will simply discuss several examples directly concerning selective transport.

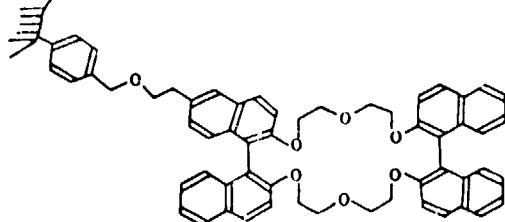
Various types of selective transport have been implemented by dissolving crown ethers in liquid membranes or by using polymers of them as polymer membranes. Examples of polymerized crown ethers are illustrated [12, 13].



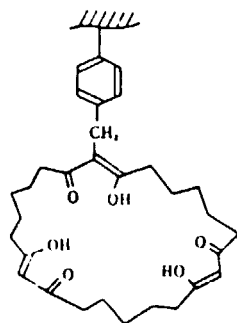
Cram has conducted optical division of amino acids and primary amines through utilization of the fact that crown ethers and primary ammonium salts have intense interaction [14]. Specifically, quantitative division of phenyl glycine by 4, in which crowns are combined with polystyrene gel, is possible. Conversely, Tabushi has extracted  $\text{UO}_2^{2+}$  from sea water using resins combined with hexaketone cyclic structures 5 [15].

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\* phonetic transliteration



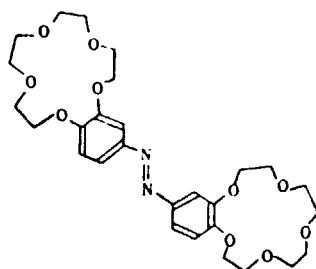
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Shinkai et al. have synthesized crown ethers containing azobenzene structures, and have discovered that incorporation of alkali metal ions differs depending on cis-trans isomerization of the azobenzene group [16]. Thus, acceleration of ionic transport can be implemented by shining light on the incorporation side of the liquid membrane system containing suitable bis crown ether 6, producing the cis form and increasing the bonding with  $K^+$ , and by maintaining the discharge side in the dark, reducing the bonding with  $K^+$ .

/482



6

Electron transport via membranes is a very important process in conversion of photo energy into chemical energy in photosynthesis. Many experiments involving activation of photosynthesis in research on models of photosynthesis have been carried out recently. One example is illustrated in figure 4.

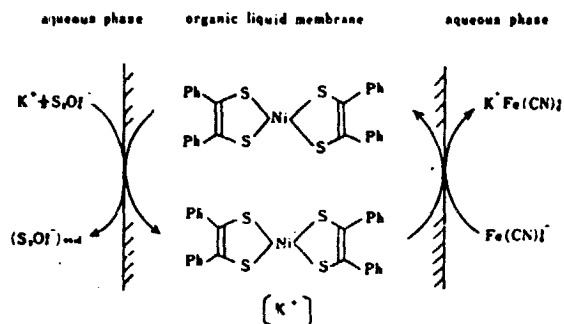


Fig. 4 Electron transport via nickel bithion.  
[ ] : crown ether

Nickel complex is the carrier in electron transport here, but  $K^+$  migration is conjugated with electron migration due to the neutralization of the charge. The rate of electron migration can be determined through changes in the cation migration rate when crown ether is added as the cation carrier. There are many explanations regarding problems in electron migration and photo energy conversion [17].

Figure 5 illustrates three basic types of membrane transport. Passive transport is migration of the substrate  $S$  due to simple diffusion, but the efficiency of this process is good due to conjugation with the external potential, such as the potential in electrodialysis, and with the pressure in reverse osmotic membranes. The second type, facilitated transport, utilizes incorporation of the transported material  $S$  by the carrier  $C$ . The aforementioned metal ion transport due to chelate



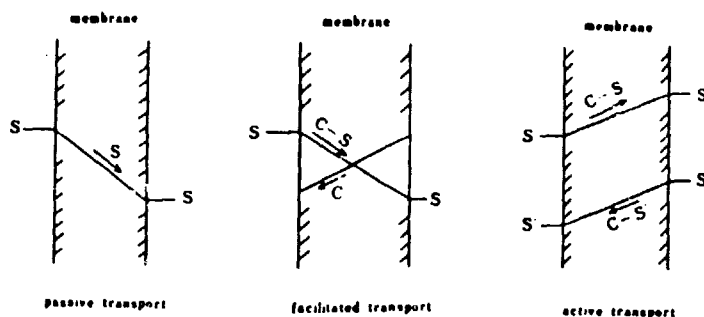


Fig. 5 Basic patterns of the membrane transport.

S: substrate C: carrier

formation and cation transport due to crown ethers both are included in this section. The transport efficiency and ionic selectivity vary with the structure of the carrier. The third type is active transport in which concentration contrary to the concentration slope is possible. Some sort of driving force must be provided to the carrier C for this purpose. When the driving force is physical potential, both reverse osmosis and electrodialysis can be considered to be active transport. However, the driving force is usually chemical potential, and a typical example of that is proton slope in biomembranes. Proton slope is the driving force in the case of concentration of metal ions due to emulsified liquid membranes illustrated in figure 3.

However, the carrier in both facilitated transport and active transport acts to promote movement in the membrane, but fixed carrier membranes in which carriers are fixed in the membrane material have the advantage of good carrier retention while the transport rate is low. Recently, lactone membranes in which lactone or its derivatives are bound to the membrane material (polymer) using pure water as the carrier have been synthesized, and active transport of metal ions could be

selectively carried out through opening or closing of the lactone rings [18]. Figure 6 illustrates the mechanism, and the driving force in this case is the proton slope. The selectivity of metal ions is determined by the  $pK_a$  of the lactone derivatives and by the hydrophobicity of the membrane. In contrast, fixed membranes utilizing tautomerism of N-hydroxyamide have been synthesized, and concentration has been conducted utilizing  $OH^-$  as the driving force.

/483

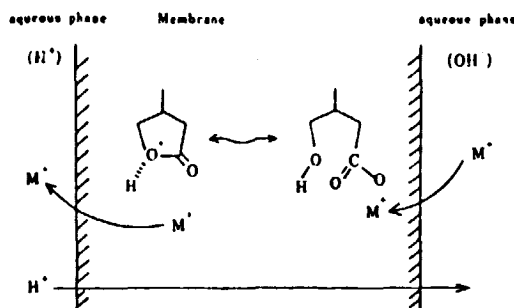
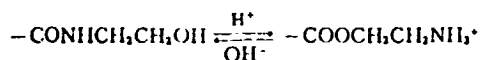


Fig. 6 Active transport of metal ions by a lactone-containing membrane.



Recently, Takagi et al. have succeeded in active transport utilizing the oxidation reduction reaction (flow of electrons) as the driving force [19].

#### 4. Biomembranes and Synthetic Bilayer Membranes

Biomembrane function is referred to greatly in designing advanced functional membranes since biomembranes provide the ideal form of functional membranes. The function of biomembranes can be summarized as illustrated in figure 7 [20]. First is reception of a physical signal, including the response of optical cells to light and the response of dermal cells to temperature and pressure. In the classification of functional polymer

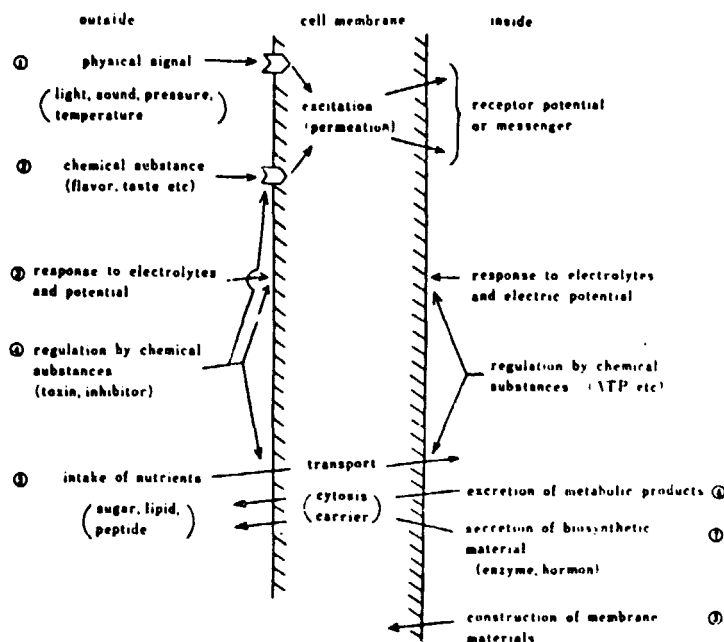


Fig. 7 Biomembrane functions.

membranes in table 1, these are the functions corresponding to (photo) conductive membranes and pyroelectric membranes. Second is the response to various chemical substances. This includes responses of gustatory cells and olfactory cells as well responses to transmitted substances such as acetylcholine and hormones. This corresponds to sensors in table 1. The third functional group involves the transport of substances, including incorporation of living substances, the excretion of metabolic products, the secretion of biosynthetic products and synthesis. Separation and permeation functions due to various types of liquid membranes and functional polymer membranes correspond to this. However, functions one to three cited above in synthetic membranes do not reach the precision attained by cellular membranes.

However, biomembranes are composed of phospholipid bilayer membranes and protein molecules buried therein, as illustrated in figure 8. Generally speaking, lipid bilayer membranes have fixed

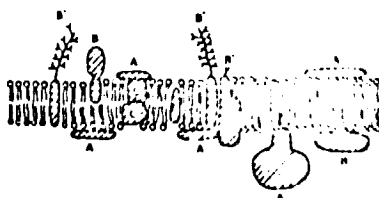


Fig. 8 Schematic illustration of biomembranes.  
A, B and C denote different types of protein molecules

substrate structures of cellular membranes and the protein molecules act as functional elements. Consequently, synthetic membranes containing protein molecules must be combined or the bilayer membrane structure must be synthetically produced to implement functions in synthetic membranes which are comparable to the functions of biomembranes. The former approach includes biosensors and bioreactors produced by combining synthetic membranes with enzymes, antibodies or microorganisms, while the latter approach involves synthetic bilayer membranes.

/484

Since bioreactors in the first approach have been introduced by Professor Hori in this special edition, we will deal with biosensors here. Highly selective sensors can be produced utilizing the great specificity of biofunctional substances such as enzymes, antibodies and receptors. As an example, we will explain the principles of enzyme sensors.

First, enzyme molecules are fixed on an appropriate matrix, as illustrated in figure 9. The matrix is divided into two types; the type in which the solid surface of metal electrodes, semi-conductor elements and piezo-electric elements is chemically modified, and the type in which enzymes are combined with membranous supports and then brought into contact with transducers. Enzymal fixation technology has already been established regarding combination of enzymes and membranous supports. The fixation of biofunctional substances other than enzymes - organelle, microorganisms, antigens, antibodies - is

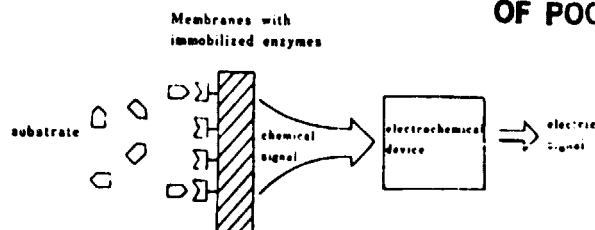


Fig. 9 Principle of enzyme sensor.

Table 4 Biosensor <sup>21)</sup>

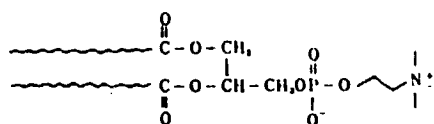
Biosensor	Receptor	Transducer	Substrate
enzyme sensor	enzyme	O <sub>2</sub> electrode H <sub>2</sub> O <sub>2</sub> electrode H <sup>+</sup> electrode CO <sub>2</sub> electrode NH <sub>3</sub> electrode	H <sub>2</sub> O <sub>2</sub> , uric acid, glucose, sugar phospholipid, cholesterol, glucose neutral lipid, penicillin amino acid urea
organella sensor	mitochondria	O <sub>2</sub> electrode	NADH
microorganism sensor	microorganism	O <sub>2</sub> electrode H <sub>2</sub> electrode H <sup>+</sup> electrode CO <sub>2</sub> electrode	glucose, acetic acid, methane, BOD BOD, formic acid cephalosporin, nicotinic acid glutamic acid, lysine
immunosensor	antigen antibody	Ag/AgCl electrode Ag/AgCl electrode O <sub>2</sub> electrode enzyme (chemical amplification)	VD antibody, blood type albumin IgG, IgA, IgM albumin, HCG, AFP

accomplished similarly. Electrochemical devices, especially various types of electrodes, are frequently used as transducers. Table 4 illustrates an example of research into biosensors summarized by Aizawa [21]. Organic compounds such as glucose, amino acids, urea, cholesterol as well as physiologically active polymers including peptid hormones and immunological globulin can be selectively measured by these sensors [22].

The lipid bilayers formed in figure 8 are phospholipid molecules, especially phosphocholine compounds (lecithin).

/485

we discovered that various types of compounds (7,8,9), including twin long chain alkyl groups, form stable bilayer membranes in water [23].



レシタン  
lecithin

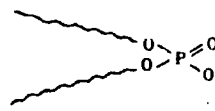


Fig. 10 Electron micrograph of synthetic bilayer membranes.

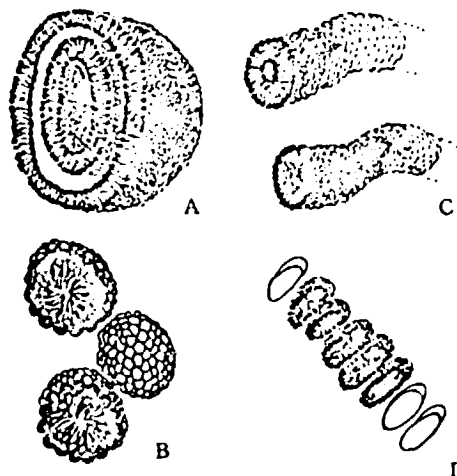


Fig. 11 Higher-order structures of synthetic bilayer membranes.

- A: multi-walled vesicle
- B: globular structure
- C: rod-like structure
- D: disk-like aggregate

Figure 10 illustrates an electron micrograph of a typical bilayer membrane. A is the endoplasmic reticulum of bilayer membranes obtained from didodecyl dimethylammonium salt. B is the lamella of a dioctadecyl dimethylammonium bilayer membrane. The thickness of a bilayer membrane is 30 to 40 Å, and corresponds to two molecular chains. The basic structure of a synthetic bilayer membrane is identical with that of a lipid bilayer membrane.

In both synthetic and lipid membranes, the constituent molecules are arranged regularly in the bilayer membrane. Membrane fluidity changes due to reversible phase transition

between gel phase and liquid crystal phase. In addition, phase separation appears in membranes composed of multiple ingredients depending on the compatibility of the various ingredients. Specifically, the basic functions of biomembranes can be reproduced even in synthetic systems since physicochemical characteristics of lipid bilayer membranes are also evident in synthetic bilayer membranes. For example, the physiological function of cellular membranes are controlled by the membrane fluidity, and the rates of various reactions including proton withdrawal, decarboxylation and acyl movement are clearly affected by phase transition and phase separation even in the case of synthetic bilayer membranes (ammonium membranes) [24].

The fluidity of biomembranes determines the selective permeability of materials. Similarly, the phase transition of synthetic bilayer membranes is applied to control of permeation. Kajiyama has produced blended membranes of polycarbonates, polyvinyl chloride and dialkyl ammonium salts [25]. In all cases, the permeability increases discontinuously due to phase transition (liquid crystal  $\leftrightarrow$  crystal).

Synthetic monolayer membranes or bilayer membranes can be composed of single chain compounds with a rigid segment, and can assume various aggregate forms as illustrated in figure 11 depending on the chemical structures of the constituent compounds. In the future, the development of various functional membranes will be possible based on these forms.

## 5. Conclusion

Above, we have introduced the present state of research into various types of functional membranes. Among these are some which have already been applied industrially and others which are in the stage of basic research. Those which are anticipated to

be applied greatly in membrane technology in organic synthetic chemistry in the 1980's are various types of selective permeable membranes and sensor membranes. The membrane material is expected to center on polymer membranes and on organic liquid membranes. In the future, functional membranes with even more superior properties will be developed if membrane structure advances due to application of bilayer membrane structures.

(received Feb. 23, 1981)



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